

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

31

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6:

H01M 10/40, 4/62

A1

(11) International Publication Number:

WO 98/26468

(43) International Publication Date:

18 June 1998 (18.06.98)

(21) International Application Number:

PCT/US97/21637

(22) International Filing Date:

8 December 1997 (08.12.97)

(30) Priority Data:

08/764,824

12 December 1996 (12.12.96)

US

(71) Applicant (for all designated States except US): VALENCE  
TECHNOLOGY, INC. [US/US]; 3111 Stonestoga Way, Hen-  
derson, NV 89015 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only):  
640 East Horizon Drive, Henderson,  
MITCHELL, Porter, H. [US/US]; 903  
Las Vegas, NV 89128 (US). BARKI,  
1770 North Green Valley Parkway #4  
89014 (US). SWOYER, Jeffrey [US/  
Avenue, Henderson, NV 89015 (US).Feng [CN/US];  
IV 89015 (US).on Rose Lane,  
any

wide

9 St

(74) Agent: KREBS, Robert, E.; Burns, Doan  
L.L.P., P.O. Box 1111, Alexandria, VA 22304-1111cker  
113-1.(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR,  
BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE,  
GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK,  
LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO,  
PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR,  
UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH,  
E, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ,  
BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE,  
CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL,  
PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN,  
ML, MR, NE, SN, TD, TG).

With

international search report.

Before the expiration of the time limit for amending the  
claims and to be republished in the event of the receipt of  
amendments.

(54) Title: POLYMER ELECTROLYTES

LITHIATED

TED ZEOLITE

(57) Abstract

A method of improving the structural integrity of p.  
optionally, inorganic fillers selected from SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>electrolytes of electrochemical cell by employing lithiated zeolites, and  
ZrO<sub>2</sub> is provided.

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

# POLYMER ELECTROLYTES CONTAINING LITHIATED ZEOLITE

## BACKGROUND OF THE INVENTION

### Field of the Invention

5 This invention relates to fabricating non-aqueous electrochemical (electrolytic) cells and, more particularly, to employing a lithiated zeolite and preferably including silica and/or alumina in the polymeric matrix of the electrolyte layer. The electrochemical cells demonstrate superior performance.

### State of the Art

10 Non-aqueous lithium ion electrochemical cells typically include an anode, a lithium electrolyte prepared from a lithium salt dissolved in one or more organic solvents and a cathode of an electrochemically active material, typically an insertion compound. During discharge, lithium ions from the anode pass through the liquid electrolyte to the electrochemically active material  
15 of the cathode where the ions are taken up with the simultaneous release of electrical energy. During charging, the flow of ions is reversed so that lithium ions pass from the electrochemically active cathode material through the electrolyte and are plated back onto the lithium anode.

20 Recently, the lithium metal anode has been replaced with a carbon anode such as coke or graphite intercalated with lithium ions to form  $\text{Li}_x\text{C}$ . In operation of the cell, lithium ion passes from the carbon through the electrolyte to the cathode where it is taken up just as in a cell with a metallic lithium anode. During recharge, the lithium ion is transferred back to the anode where  
25 it reintercalates into the carbon. Because no metallic lithium is present in the

cell, melting of the anode does not occur even under abuse conditions. Also, because lithium is reincorporated into the anode by intercalation rather than by plating, dendritic and spongy lithium growth does not occur.

5           Various factors influence the performance of electrochemical cells. For instance, the morphology of the polymeric matrix and of the polymeric binders in the anode and/or cathode can affect conductivity of the salts. Enhancement of conductivity has been demonstrated by forming porous polymeric matrices and polymeric binders. One method of producing such porous structures  
10       comprises forming polymeric structures in the presence of a plasticizer; upon extraction of the plasticizer, pores are created in the polymer. Fillers are often added to improve the strength of the polymeric matrix. However, conventional fillers while strengthening the matrix comes at the expense of reducing cell performance. In view of this, improvements are sought in the mechanical  
15       properties of the solid electrolyte and cell performance, e.g., cycle life.

#### SUMMARY OF THE INVENTION

          The present invention is based, in part, to the discovery that the use of lithiated zeolites in solid, solvent-containing electrolytes provides a beneficial  
20       increase in mechanical strength without a loss in conductivity and cumulative capacity of a solid battery. The conductivity and cumulative capacity of the solid battery is increased by the addition of a lithiated zeolite. This improvement is brought about by the ability of the lithiated zeolite to provide lithium cations. Preferably, the polymer electrolyte further includes silica,  
25       alumina, titanium dioxide, zirconium oxide, or mixtures thereof as fillers.

          The present invention is directed to electrochemical cells and methods of fabricating them wherein the non-aqueous electrolyte comprises a polymeric

matrix, the lithiated zeolites and optionally said fillers.

### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

5       The present invention is based in part on the discovery that employing fillers that include lithiated zeolite and, optionally, silica, alumina, titanium dioxide, and/or zirconium oxide significantly improves the structural integrities of the polymeric matrix of the electrolyte layer. In addition, electrochemical cells incorporating the inventive polymer electrolyte are expected to  
10 demonstrate superior electrochemical performance.

Preferred electrochemical cells include (1) a cathode comprising an active material, (2) an intercalation based carbon anode, with each electrode comprising a polymer binder and capable of reversibly incorporating (e.g.,  
15 intercalating) an alkali metal ion, and (3) a polymeric matrix containing an electrolyte solution comprising lithiated zeolite and optionally said fillers, an organic electrolyte solvent and a salt. Each electrode preferably has a current collector. Particularly preferred electrochemical cells and batteries use lithium and salts thereof.

20       Preferably, the anode comprises an anode film that is laminated onto one or both sides of a current collector which is a thin metal foil or grid. Typically, each anode film is from about 100  $\mu\text{m}$  to about 250  $\mu\text{m}$  in thickness, preferably about 110  $\mu\text{m}$  to about 200  $\mu\text{m}$ , and more preferably about 125  $\mu\text{m}$   
25 to about 175  $\mu\text{m}$ .

Similarly, preferably the cathode comprises a cathode film that is laminated onto one or both sides of the current collector *which is a thin foil or*

grid. Typically, each cathode film is from about 100  $\mu\text{m}$  to about 200  $\mu\text{m}$  in thickness, preferably about 130  $\mu\text{m}$  to about 175  $\mu\text{m}$ , and more preferably about 140  $\mu\text{m}$  to about 165  $\mu\text{m}$ .

5           The anode and cathode each also preferably includes a current collector that comprises, for example, a screen, grid, expanded metal, woven or non-woven fabric formed from an electron conductive material such as metals or alloys. Preferably, the current collector has a thickness from about 25  $\mu\text{m}$  to about 75  $\mu\text{m}$ , preferably about 35  $\mu\text{m}$  to about 65  $\mu\text{m}$ , and more preferably  
10       about 45  $\mu\text{m}$  to about 55  $\mu\text{m}$ . Each current collector is also connected to a current collector tab which extends from the edge of the current collector. In batteries comprising multiple electrochemical cells, the anode tabs are preferably welded together and connected to a copper or nickel lead. The  
15       cathode tabs are similarly welded and connected to a lead. External loads can be electrically connected to the leads. Current collectors and tabs are described in U.S. Patent 4,925,752, 5,011,501, and 5,326,653, which are incorporated  
      herein.

20       Prior to describing this invention in further detail, the following terms will be defined.

      The term "lithiated zeolite" refers to a crystalline aluminosilicate which may be represented by the empirical formula  $\text{Li}_m \text{M}_{(2-2/m)} \text{O} \cdot \text{Al}_2\text{O}_3 \cdot y\text{SiO}_2 \cdot w\text{H}_2\text{O}$ , where  $0 > m > 2$ , preferably  $1.6 \geq m \geq 1.96$ , and more preferably  
25        $1.9 \geq m \geq 1.96$ .  $y$  is an integer or non-integer 2 or greater and  $w$  is an integer representing the water contained in the voids of the zeolite.  $w$  will vary depending on the source of zeolite. Such water is shielded from the solid electrolyte and for our purposes, will not be considered part of the water

- content of the solid electrolyte. Typically,  $w$  ranges from about 0 to about 13 and preferably from about 0 to about 3.  $M$  is any suitable alkaline metal (other than lithium) or alkaline-earth metal cation that is compatible in a lithium ion electrochemical cell and preferably includes, for example, sodium or potassium and  $n$  represents the valence of the cation  $M$ . Sodium is most preferred.
- Structurally, zeolites are complex, crystalline inorganic polymers based on a framework of  $AlO_4$  and  $SiO_4$  tetrahedra linked to each other by the sharing of oxygen ions. This framework structure contains channels or interconnected voids that are occupied by cations, such as lithium ions, and water molecules.
- The cations are mobile and undergo ion exchange. The water may be removed reversibly by the application of heat which leaves intact a crystalline host structure permeated by micropores which may amount to 50% of the crystal's volume. Zeolites are widely used as drying agents to remove water. Any zeolite in lithium form is suitable for use in the present invention if (a) it is substantially lithiated, e.g. if the zeolite was synthesized in sodium form, it has been ion exchanged with a lithium salt so that the preponderance of exchangeable cations in the zeolitic voids are lithium ions; and (b) the zeolite is available as a fine particulate for inclusion in the solid electrolyte. There are many such zeolites known to the art, such as Zeolite A and Zeolite X in lithium form. In general, zeolites meeting the requirement of this invention are drawn, for example, from the group consisting of Zeolite type A, Zeolite type X, Zeolite type Y, Zeolite type L, omega, ZSM-5, chabazite, mordenite, erionite, faujasite and clinoptilolite or mixtures thereof.
- Preferably, the lithiated zeolites and fillers have a diameter of about 50  $\mu m$  or less, more preferably of about 25  $\mu m$  or less. A preferred inorganic filler is fumed silicon dioxide available as AEROSIL® R812 from Degussa AG, Frankfurt Germany. This silicon dioxide has been treated so that silanol groups

on the surface have been replaced by hydrophobic groups. The (1) lithiated zeolite or (2) blend of lithiated zeolites and one or more inorganic fillers selected from silica, alumina, titanium dioxide zirconium oxide, and mixtures thereof, typically comprises about 1% to about 30%, preferably about 5% to about 25%, and more preferably about 10% to about 20% of the polymeric electrolyte. When a blend is employed, the weight ratio of lithiated zeolite to inorganic filler(s) typically ranges from 95:5 to 10:90 and more preferably 90:10 to 50:50.

The term "plasticizer" refers to an organic solvent, with limited solubility of polymers, that facilitates the formation of porous polymeric structures. By "porous structure" is meant that upon extraction of the plasticizer the polymer remains as a porous mass. Suitable plasticizers have high boiling points typically from about 100°C to about 350°C. A number of criteria are important in the choice of plasticizer including compatibility with the components of the electrochemical cell precursor, processability, low polymer solubility and extractability by liquid solvents including, for example, diethyl ether, dimethyl ether, methanol, cyclohexane, and mixtures thereof or by supercritical fluids. Preferred plasticizers include, for example, dibutyl phthalate, dioctylphthalate, and acetates, glymes and low molecular weight polymers. The plasticizer is preferably first well mixed with a polymer and a solvent. Thereafter the plasticizer is removed by extraction and in the process the porous structure is formed. Preferably the weight ratio of plasticizer to polymer is from about 1 to about 50, more preferably about 10 to about 30, and most preferably about 20 to about 25.

The term "electrochemical cell precursor" or "electrolytic cell precursor" refers to the structure of the electrochemical cell prior to the



addition of the electrolyte solution. The precursor typically comprises (each in precursor form) an anode, a cathode, and polymeric matrix. The anode and/or cathode may each include a current collector. The polymeric matrix can function as a separator between the anode and cathode.

5

The term "activation" refers to the placement of a salt and electrolyte solvent into an electrochemical cell precursor. After activation, the electrochemical cell is charged by an external energy source prior to use.

10

The term "electrochemical cell" or "electrolytic cell" refers to a composite structure containing an anode, a cathode, and polymeric matrix with a electrolyte solution that is interposed therebetween.

15 The term "battery" refers to two or more electrochemical cells electrically interconnected in an appropriate series/parallel arrangement to provide the required operating voltage and current levels.

20 The term "a solid matrix forming monomer" refers to inorganic or organic materials which in monomeric form can be polymerized, preferably in the presence of an inorganic ion salt, lithiated zeolites, and/or fillers, and a solvent to form solid matrices which are suitable for use as solid electrolytes in electrolytic cells. Suitable solid matrix forming monomers are well known in the art and the particular monomer employed is not critical. The solid matrix forming monomers may also comprise heteroatoms capable of forming donor  
25 acceptor bonds with inorganic cations (e.g., alkali ions).

Examples of suitable organic solid matrix forming monomers include, by way of example, propylene oxide, ethyleneimine, ethylene oxide,

epichlorohydrin, acryloyl-derivatized polyalkylene oxides (as disclosed in U.S. Patent No. 4,908,283 which is incorporated herein), urethane acrylate, vinyl sulfonate polyalkylene oxides (as disclosed in U.S. Patent No. 5,262,253, which is incorporated herein), and the like as well as mixtures thereof.

- 5 Examples of suitable inorganic solid matrix forming monomers include, by way of example, phosphazenes and siloxanes. Phosphazene monomers and the resulting polyphosphazene solid matrix are disclosed by Abraham et al., Proc. Int. Power Sources Symp., 34th, pp. 81-83 (1990) and by Abraham et al., J. Electrochemical Society, Vol. 138, No. 4, pp. 921-927 (1991).

10

- The term "a partial polymer of a solid matrix forming monomer" refers to solid matrix forming monomers which have been partially polymerized to form reactive oligomers. Partial polymerization may be conducted for the purpose of enhancing the viscosity of the monomer, decreasing the volatility of the monomer, and the like. Partial polymerization is generally permitted so long as the resulting partial polymer can be further polymerized, preferably in the presence of a solvent, such as, a mixture of organic carbonate(s) to form solid polymeric matrices which are suitable for use as solid electrolytes in electrolytic cells.

20

- The term "cured" or "cured product" refers to the treatment of the solid matrix forming monomer or partial polymer thereof under polymerization conditions (including cross-linking) so as to form a solid polymeric matrix. Suitable polymerization conditions are well known in the art and include by way of example, heating the monomer, irradiating the monomer with UV light, electron beams, and the like. The resulting cured product may contain repeating units containing at least one heteroatom such as oxygen or nitrogen which is capable of forming donor acceptor bonds with inorganic cations (alkali

ions). Examples of suitable cured products suitable for use in this invention are set forth in U.S. Patent Nos. 4,830,939 and 4,990,413 which are incorporated herein.

5       The solid matrix forming monomer or partial polymer can be cured or further cured prior to or after addition of the salt, solvent, lithiated zeolite and/or fillers and, optionally, a viscosifier. For example, a composition comprising requisite amounts of the monomer or partial polymer, salt, organic carbonate solvent and viscosifier can be applied to a substrate and then cured.  
10       Alternatively, the monomer or partial polymer can be first cured and then dissolved in a suitable volatile solvent. Requisite amounts of the salt, organic carbonate solvent and viscosifier can then be added. The mixture is then placed on a substrate and cured; removal of the volatile solvent would result in the formation of a solid electrolyte. In either case, the resulting solid electrolyte  
15       would be a homogeneous, single phase product which is maintained upon curing, and does not readily separate upon cooling to temperatures below room temperature.

20       Alternatively, the solid polymeric matrix can be formed by a casting process which does not require the use of monomers or prepolymers, that is, no curing is required. A preferred method employs a copolymer of vinylidenedifluoride and hexafluoropropylene dissolved in acetone or other suitable solvent(s). Upon casting the solution, the solvent is evaporated to form the solid polymeric matrix. The solution may be casted directly onto a current  
25       collector. Alternatively, the solution is casted onto a substrate, such as a carrier web, and after the solvent (e.g., acetone) is removed, an electrode film is formed thereon.

The term "salt" refers to any salt, for example, an inorganic salt, which is suitable for use in a non-aqueous electrolyte. Representative examples of suitable inorganic ion salts are alkali metal salts of less mobile anions of weak bases having a large anionic radius. Examples of such anions are  $I^-$ ,  $Br^-$ ,  $SCN^-$ ,  $ClO_4^-$ ,  $BF_4^-$ ,  $PF_6^-$ ,  $AsF_6^-$ ,  $CF_3COO^-$ ,  $CF_3SO_3^-$ ,  $N(SO_2CF_3)_2^-$ , and the like. Specific examples of suitable inorganic ion salts include  $LiClO_4$ ,  $LiSCN$ ,  $LiBF_4$ ,  $LiAsF_6$ ,  $LiCF_3SO_3$ ,  $LiPF_6$ ,  $(CF_3SO_2)_2NLi$ ,  $(CF_3SO_2)_3CLi$ ,  $NaSCN$ , and the like. The inorganic ion salt preferably contains at least one cation selected from the group consisting of Li, Na, Cs, Rb, Ag, Cu, Mg and K.

The electrolyte typically comprises from about 5 to about 25 weight percent of the inorganic ion salt based on the total weight of the electrolyte; preferably, from about 10 to 20 weight percent; and even more preferably from about 10 to about 15 weight percent. The percentage of salt depends on the type of salt and electrolytic solvent employed.

The term "compatible electrolyte solvent" or "electrolytic solvent," or in the context of components of the non-aqueous electrolyte, just "solvent," is a low molecular weight organic solvent added to the electrolyte and/or the cathode composition, which may also serve the purpose of solvating the inorganic ion salt. The solvent is any compatible, relatively non-volatile, aprotic, relatively polar, solvent. Preferably, these materials have boiling points greater than about  $85^\circ C$  to simplify manufacture and increase the shelf life of the electrolyte/battery. Typical examples of solvent are mixtures of such materials as dimethyl carbonate, diethyl carbonate, propylene carbonate, ethylene carbonate, methyl ethyl carbonate, gamma-butyrolactone, triglyme, tetraglyme, dimethylsulfoxide, dioxolane, sulfolane, and the like. When using propylene carbonate based electrolytes in an electrolytic cell with graphite

anodes, a sequestering agent, such as a crown ether, is added in the electrolyte.

For electrochemical cells where (1) the cathode comprises lithiated cobalt oxides, lithiated manganese oxides, lithiated nickel oxides,  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ , where x is preferably about 1 and y is preferably 0.1-0.9,  $\text{LiNiVO}_4$ , or  $\text{LiCoVO}_4$ , and (2) the anode comprises carbon, the electrolytic solvent preferably comprises a mixture of ethylene carbonate and dimethyl carbonate.

The term "organic carbonate" refers to hydrocarbyl carbonate compounds of preferably no more than about 12 carbon atoms and which do not contain any hydroxyl groups. Preferred organic carbonates include, for example, aliphatic carbonates and cyclic aliphatic carbonate.

Suitable cyclic aliphatic carbonates for use in this invention include 1,3-dioxolan-2-one (ethylene carbonate); 4-methyl-1,3-dioxolan-2-one (propylene carbonate); 4,5-dimethyl-1,3-dioxolan-2-one; 4-ethyl-1,3-dioxolan-2-one; 4,4-dimethyl-1,3-dioxolan-2-one; 4-methyl-5-ethyl-1,3-dioxolan-2-one; 4,5-diethyl-1,3-dioxolan-2-one; 4,4-diethyl-1,3-dioxolan-2-one; 1,3-dioxan-2-one; 4,4-dimethyl-1,3-dioxan-2-one; 5,5-dimethyl-1,3-dioxan-2-one; 5-methyl-1,3-dioxan-2-one; 4-methyl-1,3-dioxan-2-one; 5,5-diethyl-1,3-dioxan-2-one; 4,6-dimethyl-1,3-dioxan-2-one; 4,4,6-trimethyl-1,3-dioxan-2-one; and spiro (1,3-oxa-2-cyclohexanone-5',5',1',3'-oxa-2'-cyclohexanone).

Several of these cyclic aliphatic carbonates are commercially available such as propylene carbonate and ethylene carbonate. Alternatively, the cyclic aliphatic carbonates can be readily prepared by well known reactions. For example, reaction of phosgene with a suitable alkane- $\alpha,\beta$ -diol (dihydroxy

alkanes having hydroxyl substituents on adjacent carbon atoms) or an alkane- $\alpha,\gamma$ -diol (dihydroxy alkanes having hydroxyl substituents on carbon atoms in a 1,3 relationship) yields an a cyclic aliphatic carbonate for use within the scope of this invention. See, for instance, U.S. Patent No. 4,115,206,  
5 which is incorporated herein by reference in its entirety.

Likewise, the cyclic aliphatic carbonates useful for this invention may be prepared by transesterification of a suitable alkane- $\alpha,\beta$ -diol or an alkane- $\alpha,\gamma$ -diol with, e.g., diethyl carbonate under transesterification conditions. See,  
10 for instance, U.S. Patent Nos. 4,384,115 and 4,423,205 which are incorporated herein by reference in their entirety. Additional suitable cyclic aliphatic carbonates are disclosed in U.S. Patent No. 4,747,850 which is also incorporated herein by reference in its entirety.

15 The term "viscosifier" refers to a suitable viscosifier for solid electrolytes. Viscosifiers include conventional viscosifiers such as those known to one of ordinary skill in the art. Suitable viscosifiers include film forming agents well known in the art which include, by way of example, polyethylene oxide, polypropylene oxide, copolymers thereof, and the like, having a number  
20 average molecular weight of at least about 100,000, polyvinylpyrrolidone, carboxymethylcellulose, and the like. Preferably, the viscosifier is employed in an amount of about 1 to about 10 weight percent and more preferably at about 2.5 weight percent based on the total weight of the electrolyte composition.

25 The anode typically comprises a compatible anodic material which is any material which functions as an anode in a solid electrolytic cell. Such compatible anodic materials are well known in the art and include, by way of example, lithium, lithium alloys, such as alloys of lithium with aluminum,

mercury, manganese, iron, zinc, intercalation based anodes such as those employing carbon, tungsten oxides, and the like. Preferred anodes include lithium intercalation anodes employing carbon materials such as graphite, cokes, mesocarbons, and the like. The carbon intercalation based anode precursors typically include a polymeric binder and extractable plasticizer  
5 suitable for forming a bound porous composite having a molecular weight of from about 1,000 to 5,000,000. Examples of suitable polymeric binders include EPDM (ethylene propylene diamine termonomer), PVDF (polyvinylidene difluoride), EAA (ethylene acrylic acid copolymer), EVA  
10 (ethylene vinyl acetate copolymer), EAA/EVA copolymers, and the like. The polymeric binder of the anode for the present invention preferably comprises a polymer blend which includes fluoropolymers as further described above. In one preferred embodiment, the carbon intercalation anode precursor (that is, the anode structure prior extraction) comprises from about 40 to about  
15 70 weight percent of a carbon material (e.g., graphite); from about 8 to about 20 weight percent of a polymeric binder; and from about 15 to about 40 weight percent plasticizer. The anode may also include an electron conducting material such as carbon black.

20 The cathode typically comprises a compatible cathodic material (i.e., insertion compounds) which is any material which functions as a positive pole in a solid electrolytic cell. Such compatible cathodic materials are well known in the art and include, by way of example, transition metal oxides, sulfides, and selenides, including lithiated compounds thereof. Representative materials  
25 include cobalt oxides, manganese oxides, molybdenum oxides, vanadium oxides, sulfides of titanium, molybdenum and niobium, the various chromium oxides, copper oxides, lithiated cobalt oxides, e.g.,  $\text{LiCoO}_2$  and  $\text{LiCoVO}_4$ , lithiated manganese oxides, e.g.,  $\text{LiMn}_2\text{O}_4$ , lithiated nickel oxides, e.g.,  $\text{LiNiO}_2$

and  $\text{LiNiVO}_4$  and mixtures thereof. Cathode-active material blends of  $\text{Li}_x\text{Mn}_2\text{O}_4$  (spinel) is described in U.S. Patent 5,429,890 which is incorporated herein. The blends can include  $\text{Li}_x\text{Mn}_2\text{O}_4$  (spinel) and at least one lithiated metal oxide selected from  $\text{Li}_x\text{NiO}_2$  and  $\text{Li}_x\text{CoO}_2$  wherein  $0 < x \leq 2$ . Blends can  
5 also include  $\text{Li}_y\text{-}\alpha\text{-MnO}_2$  ( $0 \leq y < 1$ ) which has a hollandite-type structure and is described in U.S. Patent 5,561,007, which is incorporated herein.

In one preferred embodiment, the compatible cathodic material is mixed with an electroconductive material including, by way of example, graphite,  
10 powdered carbon, powdered nickel, metal particles, conductive polymers (i.e., characterized by a conjugated network of double bonds like polypyrrole and polyacetylene), and the like, and a polymeric binder to form under pressure a positive cathodic plate. The polymeric binder may comprise EPDM, PVDF, EAA, EVA, or EAA-EVA copolymers, and the like. Suitable binders for use  
15 in the cathode have a molecular weight of from about 1,000 to 5,000,000. The polymeric binder of the cathode for the present invention preferably comprises a polymer blend which includes fluoropolymers as further described above.

In one preferred embodiment, the cathode is prepared from a cathode  
20 paste which comprises from about 35 to 65 weight percent of a compatible cathodic material; from about 1 to 20 weight percent of an electroconductive agent; from about 1 to 20 weight percent of a suitable polymeric binder comprising the polymer blend; from about 0 to about 20 weight percent of polyethylene oxide having a number average molecular weight of at least  
25 100,000; and from about 10 to 50 weight percent of solvent comprising a 10:1 to 1:4 (w/w) mixture of an organic carbonate and a glyme. Also included is an ion conducting amount of an inorganic ion salt. Generally, the amount of the salt is from about 1 to about 25 weight percent.



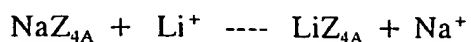
The electrolyte composition typically comprises from about 5 to about 25 weight percent of the inorganic ion salt based on the total weight of the electrolyte; preferably, from about 10 to 20 weight percent; and even more preferably from about 10 to about 15 weight percent. The percentage of salt depends on the type of salt and electrolytic solvent employed. The electrolyte composition further typically comprises from 0 to about 80 weight percent electrolyte solvent (e.g., organic carbonate/glyme mixture) based on the total weight of the electrolyte; preferably from about 60 to about 80 weight percent; and even more preferably about 70 weight percent. The electrolyte composition moreover comprises from about 5 to about 30 weight percent of the solid polymeric matrix based on the total weight of the electrolyte; preferably from about 15 to about 25 weight percent.

In a preferred embodiment, the electrolyte composition further comprises a small amount of a film forming agent. Suitable film forming agents are well known in the art and include, by way of example, polyethylene oxide, polypropylene oxide, copolymers thereof, and the like, having a numbered average molecular weight of at least about 100,000. Preferably, the film forming agent is employed in an amount of about 1 to about 10 weight percent and more preferably at about 2.5 weight percent based on the total weight of the electrolyte composition.

### METHODOLOGY

Electrochemical cells are known in the art. See, for example, U.S. Patents 5,300,373, 5,316,556, 5,346,385, 5,262,253, 4,472,487, 4,668,595, and 5,028,500, all of which are incorporated herein. The following illustrates a method of how an electrolytic cell could be fabricated with the inventive process.

Lithiated zeolites are preferably synthesized by an ion exchange process which replaces some or essentially all of the cation M in the zeolite with Li. A method of fabricating the lithiated zeolite is ion exchange using sodium or other metal cation based zeolites. For instance, zeolite type 4A (Aldrich) which is sodium based and has a particle size of less than 5  $\mu\text{m}$  can be used. Ion exchange is also applicable to lithiate other zeolites such as zeolite X described above. In this method, sodium cation in the zeolite is replaced by lithium cation as shown by the following equation, taking the sodium form of zeolite type 4A (designated  $\text{NaZ}_{4A}$ ) as the example:



Although this reaction illustrates that  $\text{Li}^+$  replaces  $\text{Na}^+$ , in practice some  $\text{Na}^+$  will remain in the zeolite. The degree of lithiation can be increased by repetitive addition of concentrated, fresh  $\text{Li}^+$  aqueous solutions until the lithium content in the zeolite reaches the desired level. Preferably, at least about 80% of sodium is replaced by lithium, more preferably about 90% and most preferably about 98%. The equilibrium of the reaction can be confirmed by atomic absorption (AA) analysis of the  $\text{Li}^+$  solution. The lithium content in the zeolite can also be determined by AA. The lithium in the zeolite can be extracted with an acid solution (e.g.,  $\text{HCl}$ ) followed by AA of the resulting solution. In this fashion, the level of lithiation can be controlled, that is, lithiated zeolite having the desired value m in the formula  $\text{Li}_m\text{M}_{(2-2/m)}\text{O} \cdot \text{Al}_2\text{O}_3 \cdot y\text{SiO}_2 \cdot w\text{H}_2\text{O}$  can be synthesized.

As an illustration of this technique, to a 500 mL beaker are added 100 g of zeolite powder and 300 mL 2M  $\text{LiCl}$  solution. The mixture is stirred until equilibrium is established as confirmed with by AA. The solid residue is

collected after filtration and mixed again with 300 mL of a fresh LiCl solution. The same procedure is repeated until the desired lithium content in the zeolite is reached. Thereafter, the wet solid is dried in a vacuum oven at 200°C before use.

5

The following illustrates a method of how an electrolytic cell could be fabricated with the inventive process. Examples 1 and 2 describe the process of preparing the anode and cathodes, respectively. Example 3 describes the procedures for fabricating a solid electrolytic cell.

10

The invention will be described using the anode and cathode structures wherein electrode materials (or films) are laminated onto both sides of the current collectors, however, it is understood that the invention is applicable to other configurations, for example, where one side of the anode and/or cathode current collector is laminated.

15

### EXAMPLE 1

The anode current collector employed is a sheet of expanded copper metal that is about 50  $\mu\text{m}$  thick. It is available under the designation 2Cu5-125 (flatten) from Delker Corp., Branford, Connecticut. The anode slurry is prepared as follows:

20

A polymer mixture comprising a copolymer of vinylidenedifluoride (VDF) and hexafluoropropylene (HFP) is prepared by mixing 6.8 grams of the copolymer in 20 grams of acetone. The copolymer (avg. MW 125K) is Kynar Flex 2801™ from Elf Atochem North America, in Philadelphia, Pennsylvania. The mixture is stirred for about 24 hours in a milling machine available from VWR Scientific, in San Francisco, California, model H-01-000. The copolymer functions as a binder for the carbon in the anode.

25

A graphite mixture is prepared separately by first adding 23.4 grams of graphite into 0.9 grams of carbon black into a solution containing 60 grams acetone, and 10.5 grams dibutyl phthalate. A preferred graphite comprises a 50:50 (by weight) mixture of a synthetic graphite available under the designation SFG-15™ from Lonza G & T, Ltd. (Sins, Switzerland) and  
5 graphitized mesocarbon microbeads available under the designation MCMB25-28™ from Osaka Gas Co., Japan. A preferred carbon black is available under the designation Super P™ from M.M.M. Carbon, Willebroek, Belgium. The graphite mixture is then vigorously mixed in a high shear mixer until a  
10 substantially homogeneous blend is formed. A suitable mixer is available from Ross Model ME100DLX, Hauppauge, New York, operating at its highest setting (about 10,000 RPM) for 30 minutes.

The anode slurry is prepared by mixing the polymer mixture and the  
15 graphite mixture together under low shear conditions to form the anode slurry wherein the components are well mixed. A portion of the acetone is allowed to evaporate from the slurry before it is laminated onto each side of the current collector. Anode films form when the remaining portion of the acetone evaporates.

20

## EXAMPLE 2

The cathode current collector employed is a sheet of expanded aluminum that is about 50  $\mu\text{m}$  thick. The aluminum grid is available under the designation 2AL5-077 from Delker Corp. The cathode slurry is prepared as  
25 follows:

A polymer mixture comprising a copolymer of vinylidenedifluoride (VDF) and hexafluoropropylene (HFP) is prepared by mixing 4.4 grams of the copolymer in 15 ml of acetone. The copolymer was Kynar Flex 2801™. The

mixture is stirred for about 24 hours in a milling jar.

5 A cathode mixture is prepared separately by mixing 28.9 grams of  $\text{LiMn}_2\text{O}_4$ , 2.4 grams of carbon black (Super P™) into a solution containing 60 grams acetone, and 8.7 grams dibutyl phthalate. The mixture is then vigorously mixed in the a high shear mixer until a substantially homogeneous blend is formed.

10 The cathode slurry is prepared by mixing the polymer mixture and the cathode mixture together under low shear conditions to form the cathode slurry wherein the components are well mixed. A portion of the acetone is allowed to evaporate from the slurry before it is laminated onto each side of the current collector. Cathode films form when the remaining portion of the acetone evaporates.

15 The above anode and cathode films are formed directly on the current collector by laminating the slurry mixtures onto the current collector surfaces. Alternatively, each film can be prepared by first casting a slurry onto a substrate or carrier web and allowing the solvent to evaporate thus leaving the film. Thereafter, the films can be laminated onto each side of the current collector.

### EXAMPLE 3

25 A solid electrochemical cell is prepared by first positioning a polymeric matrix between the anode and cathode and thereafter fusing the structures under moderate pressure and temperature (e.g.,  $130^\circ\text{C}$ ) to form an electrochemical cell precursor. The polymeric matrix is formed by casting a polymeric slurry comprising acetone, dibutyl phthalate, lithiated zeolite (and optionally a filler

such as fumed SiO<sub>2</sub>), and the VDF/HFP copolymer on a suitable substrate or carrier web and allowing the acetone to evaporate. No curing by radiation is required. It is believed that the lithiated zeolite and/or filler assists the activation process by creating physico-chemical conditions such that the electrolyte solution quickly and completely fills the pores created by the extraction of the dibutyl phthalate. Preferably, the polymeric slurry is mixed under low shear conditions as not to degrade the copolymer.

Preferably in preparing the polymer mixture for both the anode and cathode slurries is that the polymer (or copolymer) not be subject to high shear so as to be degraded. Furthermore, preferably the polymer or copolymer employed has a high average molecular weight. Preferably the average molecular weight is between 50 K to 750 K, more preferably 50 K to 200 K, and most preferably 50 K to 120 K. Furthermore, it is preferred that polymer or copolymer has a narrow molecular weight have range. Preferably

$$\frac{M_n}{M_w} \sim 1.0$$

Next the dibutyl phthalate plasticizer is extracted from the precursor. Extraction can be accomplished using conventional organic liquid solvents such as diethyl ether or by a dense fluid or gas which refers to a gas compressed and heated to either supercritical or subcritical conditions to achieve liquid-like densities. Dense gases and fluids are known in the art. See, for example, U.S. Patents 5,013,366, 5,267,455, 4,219,333, 4,012,194, and 3,969,196, which are incorporated herein. A preferred dense gas is carbon dioxide. The precursor is than pre-packaged in moisture-impermeable material which is described, for example, in U.S. Patent 5,326,653 which is incorporated herein, before being

activated. Activation preferably occurs in an inert (e.g., argon) atmosphere. Finally, the packaging of the electrochemical cell is sealed.

5 While the invention has been described in terms of various preferred embodiments, the skilled artisan will appreciate the various modifications, substitutions, and changes which may be made without departing from the spirit hereof. The descriptions of the subject matter in this disclosure are illustrative of the invention and are not intended to be construed as limitations upon the scope of the invention.

10

WHAT IS CLAIMED IS:

1. An electrolytic cell which comprises:  
an anode; a cathode; and interposed therebetween a solvent-containing  
5 electrolyte which comprises:  
a polymeric matrix;  
a salt;  
a solvent; and  
a lithiated zeolite.  
10
2. The electrolytic cell of Claim 1 wherein the electrolyte further  
comprises an inorganic filler that is selected from the group consisting of  $\text{SiO}_2$ ,  
 $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}$ , and mixtures thereof.
- 15 3. The electrolytic cell of Claim 1, wherein said inorganic filler is  
hydrophobic  $\text{SiO}_2$ .
4. The electrolytic cell of Claim 1, wherein said inorganic filler is  
 $\text{Al}_2\text{O}_3$ .  
20
5. The electrolytic cell of Claim 1, wherein the lithiated zeolite  
comprises from about 1% to about 30% by weight of the electrolyte.
6. The electrolytic cell of Claim 2, wherein the weight ratio of  
25 lithiated zeolite to inorganic filler ranges from about 95:5 to about 10:90.
7. The electrolytic cell of Claim 2, wherein the lithiated zeolite and  
inorganic filler comprise from about 1% to about 30% by weight of the



electrolyte.

8. The electrolytic cell of Claim 1, wherein the lithiated zeolite has the empirical formula  $\text{Li}_m\text{M}_{(2-2/n)} \cdot \text{O} \cdot \text{Al}_2\text{O}_3 \cdot y\text{SiO}_2 \cdot w\text{H}_2\text{O}$ , where M is an alkaline metal, other than lithium, or alkaline-earth metal, n is the valence of M and is equal to 1 or 2,  $0 > m > 2$ , y is an integer or non-integer 2 or greater, and w is an integer from about 0 to about 13.

9. The electrolytic cell of Claim 8 wherein the M is sodium.

10. The electrolytic cell of Claim 9 wherein  $1.6 \geq m \geq 1.96$ .

11. The electrolytic cell of Claim 1 wherein the anode comprises an intercalation based anode comprising carbon.

12. The electrolytic cell of Claim 1 wherein the cathode comprises material selected from the group consisting of vanadium oxide, lithiated manganese oxide, lithiated nickel oxide, lithiated cobalt oxide, and mixtures thereof.

13. The electrolytic cell of Claim 12, wherein the anode comprises an intercalation based anode comprising carbon.

14. A process for preparing an electrolytic cell which comprises:  
(a) providing a cathode;  
(b) providing an anode;  
(c) forming an electrolyte between the cathode and anode wherein the electrolyte comprises:

a polymeric matrix,  
a salt,  
a solvent; and  
a lithiated zeolite.

5

15. The process of Claim 14 wherein the electrolyte further comprises an inorganic filler that is selected from the group consisting of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and mixtures thereof.

10 16. The process of Claim 14, wherein said inorganic filler is hydrophobic  $\text{SiO}_2$ .

17. The process of Claim 14, wherein said inorganic filler is  $\text{Al}_2\text{O}_3$ .

15 18. The process of Claim 14, wherein the lithiated zeolite comprises from about 1% to about 30% by weight of the electrolyte.

19. The process of Claim 15, wherein the weight ratio of lithiated zeolite to inorganic filler ranges from about 95:5 to about 10:90.

20

20. The process of Claim 15, wherein the lithiated zeolite and inorganic filler comprise from about 1% to about 30% by weight of the electrolyte.

25 21. The process of Claim 14, wherein the lithiated zeolite has the empirical formula  $\text{Li}_m\text{M}_{(2-2/n)} \cdot \text{O} \cdot \text{Al}_2\text{O}_3 \cdot y\text{SiO}_2 \cdot w\text{H}_2\text{O}$ , where M is an alkaline metal, other than lithium, or alkaline-earth metal, n is the valence of M and is equal to 1 or 2,  $0 < m < 2$ , y is an integer or non-integer 2 or greater, and w

is an integer from about 0 to about 13.

22. The process of Claim 21 wherein M is sodium.
- 5 23. The process of Claim 22 wherein  $1.6 \geq m \geq 1.96$ .
24. The process of Claim 14 wherein the anode comprises an intercalation based anode comprising carbon.
- 10 25. The process of Claim 14 wherein the cathode comprises material selected from the group consisting of vanadium oxide, lithiated manganese oxide, lithiated nickel oxide, lithiated cobalt oxide, and mixtures thereof.
- 15 26. The process of Claim 25 wherein the anode comprises an intercalation based anode comprising carbon.

# INTERNATIONAL SEARCH REPORT

Inte .lonal Application No

PCT/US 97/21637

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 H01M10/40 H01M4/62

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	SLANE S ET AL: "COMPOSITE GEL ELECTROLYTE FOR RECHARGEABLE LITHIUM BATTERIES" JOURNAL OF POWER SOURCES, vol. 55, no. 1, 1 May 1995, pages 7-10, XP000541728 see the whole document ---	1,5, 11-14, 18,24-26
Y	PATENT ABSTRACTS OF JAPAN vol. 096, no. 002, 29 February 1996 -& JP 07 262999 A (TOPPAN PRINTING CO LTD), 13 October 1995, see abstract ---	1,5, 11-14, 18,24-26
X	EP 0 557 250 A (ENEA ENTE NUOVE TEC) 25 August 1993 see the whole document ---	1
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

7 April 1998

Date of mailing of the international search report

23/04/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

De Vos, L

# INTERNATIONAL SEARCH REPORT

Int'l. Application No  
PCT/US 97/21637

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 102 (E-1511), 18 February 1994 & JP 05 303980 A (YUASA CORP), 16 November 1993, see abstract	1, 14
P, X	EP 0 774 795 A (ENIRICERCH SPA ;OLIVETTI PERSONAL COMP SPA (IT)) 21 May 1997 see page 2, line 26 - page 3, line 26	1, 11-14, 18, 24-26
X	N.MUNICHANDRAIAH: "influence of zeolite on electrochemical and physicochemical properties of polyethylene oxide solid electrolyte" JOURNAL OF APPLIED ELECTROCHEMISTRY, vol. 25, pages 857-863, XP002061687, see page 857, column 1, paragraph 1 - column 2, paragraph 3 see page 860, column 1, paragraph 1 - page 862, column 2, paragraph 2	1
A	PATENT ABSTRACTS OF JAPAN vol. 008, no. 194 (E-264), 6 September 1984 -& JP 59 081869 A (HITACHI MAXELL KK), 11 May 1984, see abstract	1, 8, 21
A	PATENT ABSTRACTS OF JAPAN vol. 007, no. 208 (E-198), 14 September 1983 & JP 58 103776 A (SANYO DENKI KK), 20 June 1983, see abstract	1
A	WO 95 15589 A (BELL COMMUNICATIONS RES) 8 June 1995 see page 7, line 12-29; claims 1-4	2-4, 15-17
A	PATENT ABSTRACTS OF JAPAN vol. 009, no. 099 (E-311), 27 April 1985 & JP 59 224071 A (FUJI DENKI KAGAKU KK), 15 December 1984, see abstract	1, 8-10, 21-23
A	PATENT ABSTRACTS OF JAPAN vol. 011, no. 133 (C-418), 25 April 1987 & JP 61 268636 A (TORAY IND INC), 28 November 1986, see abstract	8-10, 21-23

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/21637

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0557250 A	25-08-93	IT 1254709 B CA 2087454 A US 5576115 A	09-10-95 18-07-93 19-11-96
EP 0774795 A	21-05-97	IT MI952369 A JP 9180706 A	19-05-97 11-07-97
WO 9515589 A	08-06-95	US 5460904 A CA 2177361 A DE 737369 T EP 0737369 A JP 9500485 T US 5478668 A US 5456000 A US 5540741 A US 5470357 A US 5587253 A US 5571634 A	24-10-95 08-06-95 13-02-97 16-10-96 14-01-97 26-12-95 10-10-95 30-07-96 28-11-95 24-12-96 05-11-96